APPLYING A MIXED BED ION EXCHANGE COLUMN SIMULATOR TO RADWASTE SYSTEMS

D. Hussey
EPRI

G. Foutch
Oklahoma State University

Y. Jia
Oklahoma State University

ABSTRACT

A BWR liquid radwaste demineralizer is modeled using the Oklahoma State University Mixed Bed Ion Exchange simulator. Three scenarios are modeled: normal operations, organically fouled resin, and the effects of an air intrusion.

The results show that fouled resin impacts the removal of cobalt-60 greatly; however, the air intrusion has much less pronounced effects on activity removal. The predictions indicate that conductivity is not a suitable measurement to determine if a demineralizer should be taken out of service.

INTRODUCTION

Liquid radwaste demineralizers often face challenges caused by environmental variables such as organic fouling or air intrusions. The complex chemistry inside a mixed bed prevents accurate estimation of the effects of outside disturbances using standard engineering rule-of-thumb analysis techniques. This paper applies a mathematical model to provide insight into the internal chemistry dynamics of the radwaste demineralizer. For information about the OSUMBIE mixed bed model, contact Dr. Gary Foutch at foutch@okstate.edu, (405) 744-9113.

Model Description

The Oklahoma State Mixed Bed Ion Exchange (OSUMBIE) model has been in development for 20 years (1). Initially, the model provided solutions to simple sodium-chloride systems, but over the years the model has developed into multi-component simulator with the capability to model complex chemistry and fixed bed dynamics. A complete mathematical description of the model is beyond the scope of this paper, but the four concepts that drive the model are the application of solution equilibrium, reaction equilibrium, and mass transfer models combined in a column material balance. Each concept is described below.

Solution equilibrium—OSUMBIE assumes ideal solution thermodynamics with dependent temperature dissociation constants. Weak electrolyte concentrations are calculated using common thermodynamic relationships available in most chemistry textbooks.

Reaction equilibrium—The ion exchange equilibrium model is based on the well-known law of mass action where the concentrations of the products divided by the concentrations of the
reactants is equal to a constant. The equation for a single ion pair A-B is shown in Equation 1, where \( q \) is the resin phase concentration, and \( C \) is the solution phase concentration of species \( i \). Selectivity data are taken from the EPRI Ion Exchange database.

\[
K_A^{B} = \left( \frac{q_A}{C_A} \right)^{z_B} \left( \frac{C_B}{q_B} \right)^{z_A}
\]

(Eq. 1)

Mass transfer—When ion concentrations are below 0.02 N, experimental evidence has indicated that the rate limiting step of ion exchange is diffusion of ions across the stagnant film surrounding the resin bead. The Nernst-Planck film diffusion model, which includes concentration gradient and electric potential in the flux expression, is used to calculate the mass transfer rates entering and leaving the ion exchange resin. The film thickness is calculated using a mass transfer coefficient correlation.

Column material balance—Solution equilibrium, reaction equilibrium, and mass transfer are used to describe the relationship between water and individual resin beads; however, modeling mixed bed performance requires transient differential equations to combine these relationships as a function of time and distance through the bed.

The column material balance equations are derived from well-known fixed bed mass transport equations that assume no axial or radial dispersion for each exchanging species. The equations are integrated numerically, with the dissociation, reaction, and flux expressions calculated at each time and distance node. A mathematical description of the calculation is complex and not discussed in this paper. The key concepts of the relationships between the solution and resin concentrations as a function of specie, time and distance \((x_{i,j,k}, y_{i,j,k})\) applied in a dimensionless time \((\tau)\) and distance \((\xi)\) integration are summarized below in Fig. 1.

![Graphical depiction of the numerical integration of a column material balance](image)

Fig. 1. Graphical depiction of the numerical integration of a column material balance
RADWASTE SYSTEM AND PROBLEM DESCRIPTION

A BWR radwaste mixed bed demineralizer was chosen for analysis. The following system assumptions were made. These properties were not varied throughout the scenarios.

Table I. Bed Parameters used for Simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed depth (m)</td>
<td>0.91</td>
</tr>
<tr>
<td>Bed diameter (m)</td>
<td>1.52</td>
</tr>
<tr>
<td>Flow rate (Liters/min)</td>
<td>378.5</td>
</tr>
<tr>
<td>Cation resin fraction</td>
<td>0.41</td>
</tr>
<tr>
<td>Anion resin fraction</td>
<td>0.59</td>
</tr>
<tr>
<td>Resin void fraction</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The following contaminants were assumed for the evaluation. For simplicity, the only radioactive contaminant chosen for the analysis was cobalt-60. The specific activity of cobalt-60 is 1132 Ci/g, which was used to calculate the concentration of cobalt in parts per billion.

Table II. Contaminant Concentrations and Initial Loadings used for Simulation

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Concentration ppb(µCi/mL)</th>
<th>Initial Loading (equiv.contaminant/total equivalents)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Sulfate</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Silica (as H₃SiO₄)</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Cobalt (Co⁺)</td>
<td>0.0018 (2.0e-3)</td>
<td>0</td>
</tr>
<tr>
<td>Sodium</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>Carbonate</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Initial loading is the fraction of the exchange sites used by the contaminant. For liquid radwaste systems, resins are not regenerated and the assumption is made that the initial loading of all contaminants is zero.

OSUMBIE provides reasonable estimates of the effluent concentrations given appropriate inputs, but the full potential of the model is achieved through relative comparisons. Three operating scenarios were modeled for this paper: 1) Normal operations, 2) Organically fouled resins, and 3) Substantial air intrusion. Each of the cases is described below.

Normal Operations

As implied, normal operations assumes typical operation using the influent concentrations listed in Table II. This simulation provides a baseline for comparison to the other two simulations, and it is not intended to be representative of all BWRs.
Organically Fouled Resin

A common concern in BWR liquid radwaste systems is organic fouling of the resin. The two primary issues are the disposal costs of resin and the effluent quality must remain high because the discharge is often released back into the steam circuit.

Fouled resin is modeled by reducing the mass transfer coefficient (MTC). The MTC has units of velocity, and it represents the average velocity of a contaminant molecule across a stagnant film between the bulk solution and the surface of the resin. Reducing the mass transfer coefficient does not reduce the capacity of the resin, but it slows the exchange of the contaminant. Therefore, it is more likely for the contaminants to be ‘pushed’ through the bed before they have time to exchange. For these simulations, the mass transfer coefficient was reduced to 60% of the theoretical value.

Substantial Air Intrusion

During a recent situation in a nuclear plant had indicated that a vacuum seal had failed and allowed a majority of the bed to be exposed to air. Air contains carbon dioxide, and when moist anion resin is exposed to air, it was assumed the resin will be loaded with carbonic acid. The plant had to justify the continued operation of the bed even though the conductivity was higher than predetermined limits. This scenario assumes an air saturated bed that loads the anion resin with 90% bicarbonate.

RESULTS

Fig. 2 shows the relative effluent cobalt activities for the three operating scenarios. It is clear that the fouled resin has the worst performance, but it is noteworthy that the air intrusion has very little effect on the effluent cobalt activity. This is explained by observing cobalt is assumed to be in the divalent oxidation state, and has a very high selectivity for the cation resin. The air intrusion has a slightly lower pH throughout the bed, which will impede cobalt transfer slightly, but the anion resins and contaminants have very little effect on the cation transfer. Note the air intrusion conductivity (Fig. 3) is much higher than the other scenarios, which is attributed to carbonate (Fig. 4). This shows that conductivity, while a good indicator that the resin may be saturated with a contaminant, should not be used as the only measurement to determine that a bed should be removed from service. Gamma spectroscopy and ion chromatography should be used to determine if a bed is exhausted.

As expected, fouled resin had a significant impact on cobalt removal. The expected release activity is three orders of magnitude higher than the normal or air intrusion scenarios. However, the difference was not noticeable in the conductivity. This is expected because of the very low influent concentrations of the contaminants. Carbonate is removed to sub-ppt concentrations, which is well below observable conductivity (usually 0.5 ppb or higher is needed for conductivity measurements).
Fig. 2. Comparison of cobalt effluent activity for three operating scenarios.

Fig. 3. Comparison of effluent conductivity for three operating scenarios.
Fig. 4. Comparison of effluent carbonate concentrations for three operating scenarios

CONCLUSIONS

A simple operating case of a BWR liquid radwaste system has been modeled with the Oklahoma State University Mixed Bed Ion Exchange model. The results indicate that organic fouling of the resin can significantly impact the activity removal because fouling impedes the very low driving force. Air intrusions have little effect on activity removal because the interaction between anion resin and cation resin is only affected by the pH changes in the bed, which did not affect the cobalt removal because of the strong selectivity of the cobalt ion for the cation resin.

REFERENCES